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Title: Plutonium particle analysis by LG-SIMS and LA-MC-ICP-MS for environmental safeguards

Author(s): Denton, Joanna S.
Tenner, Travis Jay
Williamson, Todd L.
Lamont, Stephen Philip
Steiner, Robert Ernest

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Plutonium particle analysis by LG-SIMS and LA-MC-ICP-MS for environmental safeguards

Project Categories

24.1.3.4 Standards & Infrastructure
☐ or 4.1 NWAL Improvements
☐
☐ or ☐

PROPOSED STATEMENT OF WORK

Abstract

During nuclear facility inspections, International Atomic Energy Agency (IAEA) inspectors collect dust particles using cotton swipes. Analysis of these swipes is an extremely powerful tool with which to confirm treaty compliance or identify treaty violations. Through particle analysis it is possible to identify individual particles representative of nuclear activities. Uranium particle analysis is a reasonably mature technique used by IAEA and its Network of Analytical Laboratories for treaty verification. However, the IAEA has recently identified the maturation of plutonium and mixed uranium-plutonium particle analysis techniques as a **top priority**. We propose to address this area directly by developing the new methods necessary to analyze samples containing plutonium and mixed uranium-plutonium particles. The end products of this study will be: (A) more accurate and ultra-precise isotopic characterization of plutonium-bearing particles from environmental swipe samples, and (B) development and validation of laser ablation particle analysis techniques as robust and accurate analysis methodologies for future safeguards missions.

Mission Relevance

The primary goal of international safeguards is to verify compliance with treaty obligations. Such treaties deter the proliferation of nuclear weapons - a core national and international security aim. One component of modern-day safeguards is environmental sampling. This involves the collection of dust particulates from nuclear facilities by wiping surfaces with cotton swipes (see Fig. 1).

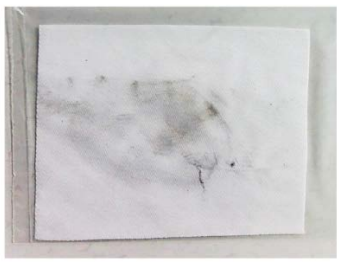


Figure 1. Cotton swipe

Analysis of such swipes is carried out by the IAEA and its Network of Analytical Laboratories (NWAL). This analysis takes the form of *bulk analysis* (measuring the U and Pu isotopic signatures of the entire sample) or *particle analysis* (separating and characterizing individual particles in order to determine their unique isotopic signature (see Fig. 2)).

Bulk analysis yields an average isotopic composition of all particles. In contrast, particle analysis is capable of identifying individual or groups of particles that may indicate nuclear activity hidden amongst a vast range of samples consistent with the State's declaration. Therefore particle analysis is usually considered the more powerful approach.[1,2]

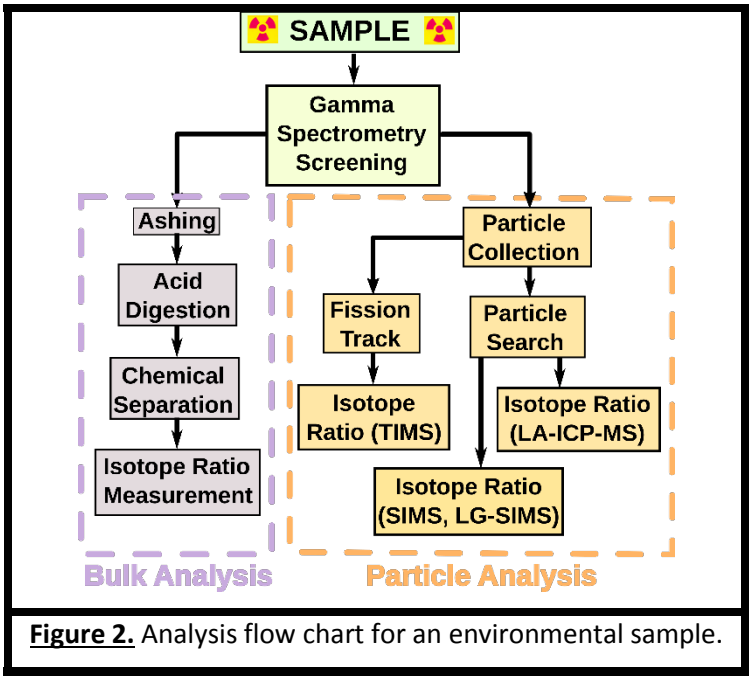


Figure 2. Analysis flow chart for an environmental sample.

Isotopic analysis of isolated uranium particles is generally carried out by Fission Track Thermal Ionization Mass Spectrometry (FT-TIMS)[e.g.1], Secondary Ionization Mass Spectrometery (SIMS),[e.g.1,3] and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)[e.g.1,4] (Figure 2). However, the isotopic analysis of plutonium and mixed uranium-plutonium particles has only recently been attempted using SIMS[5,6] and LA-ICP-MS[7].

The IAEA recently identified the maturation of plutonium and mixed uranium-plutonium particle analysis techniques as a **TOP PRIORITY**[8,9] (e.g. Develop and Implement the Laser Ablation ICP-MS technique, and develop capabilities to use a large-geometry secondary ion mass spectrometer (LG-SIMS) for accurate and precise measurement of the isotopic composition of uranium/plutonium[9]). This is in support of priority objective T.2 and R&D need R6[9] - the "*isotopic characterization of Pu containing particles using FT-LAICPMS and LGSIMS*".[9] The development of such technology and analysis methods will be carried out in this project.

Scope of Work

Through a NA-22 effort, measurement protocols for analysing mixed uranium-plutonium particles with LG-SIMS are being researched. That work will compliment and inform portions of the LG-SIMS work in this proposal. We will develop and validate new plutonium (and for LA-MC-ICP-MS mixed uranium-plutonium) particle isotopic analysis techniques using both LA-MC-ICP-MS and LG-SIMS. These methods will advance the NWAL's environmental sample analysis capability. The Nuclear and Radiochemistry (C-NR) group at Los Alamos National Laboratory (LANL) is currently involved in ongoing bulk analysis of environmental safeguards swipes as part of NWAL. As our laboratory has both LG-SIMS and LA-MC-ICP-MS instruments, it is uniquely positioned to support NWAL particle analysis R&D. Our laser unit uses a CO_2 gas source to generate a 193 nm laser beam and this wavelength is desirable because it results in a more consistent amount of each element ablated over time. The spot size of the laser beam can be reduced to <10 µm resulting in the ability to analyze individual particles. The laser will be connected to a ThermoScientific Neptune Plus MC-ICP-MS equipped with both Faraday and SEM detectors enabling the accurate and precise simultaneous measurement of isotopic ratios.

Our LG-SIMS instrument is a Cameca IMS 1280, identical to the IAEA's instrument at the Seibersdorf Analytical Laboratory. The ion detection system has multiple collectors, allowing for up to 5 different isotope/isotopologue masses to be counted simultaneously. Our LG-SIMS is equipped with Automated

Particle Measurement software (APM)[10] that produces maps of particles dispersed over a rastered analysis region, and determines isotope ratios of individual particles from within the analyzed region. For a typical sample, several hundreds to thousands of individual particle isotope ratios are collected, providing a representative dataset. We prepare samples so that the majority of particles are evenly spaced, with typical distances of 5 to 25 microns per particle. Accordingly, we adjust our primary beam current to maximize the detector counts over a given rastered analysis area (~200,000 counts per second).

The LG-SIMS at LANL is an already proven capability for the isotopic analysis of uranium particles for nuclear forensics applications (see Fig. 3). Therefore, the first task will be to establish an actinide particle analytical protocol using our LA-MC-ICP-MS capability. The laser ablation protocols will then be validated using LANL in-house (well-characterized) samples and reference materials already measured by the LANL LG-SIMS. This will allow us to benchmark our LA-MC-ICP-MS capability against the more widely-used LG-SIMS technique for actinide particle analysis. Powdered plutonium reference materials (e.g. CRM126A and well-characterized LANL plutonium materials) will also be analyzed by LG-SIMS and subsequently by LA-MC-ICP-MS. At this point, an assessment of the success, in terms of accuracy and precision, of the plutonium-only particle analysis results will be made. This assessment will define the scope of the following tasks. We anticipate subsequent analysis of particles containing both uranium and plutonium, in particular for understanding applications to characterize spent nuclear fuel. The over-arching goals for the project are: (A) more accurate and ultra-precise isotopic characterization of plutonium-bearing particles from environmental swipe samples, and (B) development and validation of laser ablation particle analysis techniques as a robust and accurate analysis methodology for future safeguards missions.

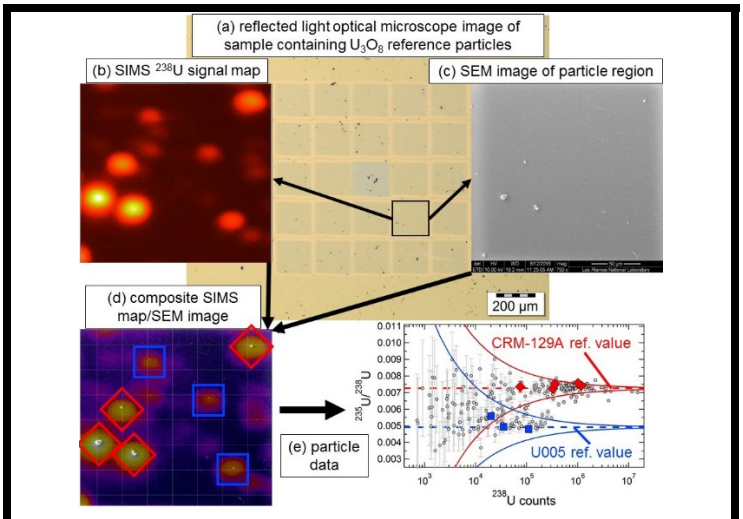


Figure 3. LANL SIMS example analysed mix of CRM-129A and U005 reference U_3O_8 particles. (a) Optical microscope image showing 25 rastered analyses (squares) collected. (b & c) SIMS ^{238}U signal map and respective SEM image of a single analysed area. (d) Composite image, overlaying those from (b & c). (e) All particle $^{235}U/^{238}U$ data (*n*: 233). Red and blue error envelopes for CRM-129A and U005 (respectively) are based on counting statistics, modeled from single reference material sample analyses; in terms of ^{238}U counts (x-axis) they show where CRM-129A and U005 particles can and cannot be resolved. Highlighted red diamonds and blue squares correspond to particles from image (d), and are consistent with the reference values for CRM-129A and U005, respectively. U005 particles appear smaller than CRM-129A particles.[12]

The results of our study will be made available through reports and presentations to the DOE and other interested stakeholders in coordination with DOE. Additionally, with DOE approval we will publish the

results to the international community in one or more peer-reviewed scientific articles. All necessary experimental facilities are available at LANL/C-NR to carry out the proposed work, and all necessary samples are in-house. The project is inherently low-risk.

Project Trajectory

Task 1 (FY1): Establishment of actinide particle isotopic analytical protocols using LA-MC-ICP-MS and benchmarking against LG-SIMS using same sample(s). Milestone = validated LA-MC-ICP-MS actinide particle isotopic analytical protocol. Deliverable = unclassified report to NA-241 and publication submitted for peer-review.

Task 2 (FY1): Prepare mounts containing particles of plutonium. Isotopic measurement of plutonium mounts by LG-SIMS and LA-MC-ICP-MS. Milestone: comparison of LG-SIMS and LA-MC-ICP-MS measurement capability for the isotopic analysis of samples containing plutonium particles. Decision point = success of plutonium-only particle measurements will define the scope of Task 3. Deliverable = unclassified report to NA-241 and publication submitted for peer-review.

Task 3 (end of FY1 and FY2 if funded): Prepare and analyse mounts containing uranium and plutonium-bearing particles; measurement by LG-SIMS followed by LA-MC-ICP-MS. Milestone = comparison of LG-SIMS and LA-MC-ICP-MS measurement capability for the isotopic analysis of samples containing uranium and plutonium-bearing particles. Deliverable = unclassified report to NA-241 and publication submitted for peer-review.

Participating Laboratories

Principal Investigator Table

Lab	Lab Program Manager	Principal Investigator	PI's Email	PI's Phone
Los Alamos National Laboratory	Holly Trellue	Joanna Denton, Travis Tenner	jdenton@lanl.gov, tenner@lanl.gov	505-695-3705, 505-664-0115

Summary Table

Task No.	Event Type	Event Title	Responsible Lab	Event Date
1	Milestone	Benchmark of LA-MC-ICP-MS uranium particle analysis against LG-SIMS measurement	LANL	04/01/2019
	Deliverable	Unclassified report	LANL	05/01/2019
	Publication	Submission of peer-reviewed manuscript	LANL	07/01/2019
2	Milestone	Preparation of plutonium particle mount and analysis by LG-SIMS	LANL	05/01/2019
	Milestone	Analysis of plutonium particle mount by LA-MC-ICP-MS	LANL	07/01/2019
	Deliverable	Unclassified report	LANL	08/01/2019
	Publication	Submission of peer-reviewed manuscript	LANL	010/01/2019
	Decision point	Decide scope of task 3 based on success of measuring Pu-only mounts	LANL	07/01/2019

3	Milestone	Preparation of mixed plutonium-uranium particle mounts and analysis by LG-SIMS	LANL	01/01/2020
	Milestone	Analysis of mixed plutonium-uranium particle mounts by LA-MC-ICP-MS	LANL	03/01/2020
	Deliverable	Unclassified report	LANL	04/01/2020
	Publication	Submission of peer-reviewed manuscript	LANL	06/01/2020

Pertinent references

[1]**Hubert et al., 2014**. Spectro. Chim. Acta B, 93, 52-60.

[2]**Donard et al., 2016.** J. Anal. At. Spectrom., 32, 96-106.

[3]**Hedberg et al., 2016**. J. Anal. At. Spectrom., 30, 2516-2524.

[4]**Pointurier et al., 2011.** Anal. Chem., 83, 7841-7848.

[5]**Ranebo et al., 2010.** Anal. Chem., 82, 4055-4062.

[6]**Esaka et al., 2011.** Mass Spec. Letters, 2, 80-83.

[7]**Konegger-Kappel and Prohaska, 2016**. Anal. Bioanal. Chem., 408, 431-440.

[8]**IAEA STR-386**. IAEA Development and Implementation Support Programme for Nuclear Verification 2018-2019 document.

[9]**IAEA STR-385**. Research and Development Plan 2018-2019 document.

[10]**Hedberg et al., 2010**. J. Anal. At. Spectrom., 26, 406-413.

[11]**Tenner, 2018.** LA-UR-18-21145

Plutonium particle analysis by LG-SIMS and LA-MC-ICP-MS for environmental safeguards

Associated Work

Project Title	Funding Agency	Years funded
Uranium/plutonium particle analysis by LG-SIMS and LA-MC-ICP-MS	DOE NA-241, SGTec	FY 2019 proposal
Reactor Venture	DOE/NNSA NA-221, Pu Production Portfolio	FY14 – FY20
NTNFC Early Career Award	NTNFC/DHS	FY18 - FY19

Reactor Venture: Large multi-year, multi-disciplinary project. Aspects of the Reactor Venture project related to the proposed work here are related to SIMS analysis. Two of the goals of the SIMS work in the Reactor Venture are 1) to understand ionization differences between U and Pu in mixed samples and 2) mitigate hydride interferences that complicate U and Pu measurements in mixed samples. The work proposed here would complimentarily build off of the Reactor Venture work, extending the range of samples studied to include environmental, particulate samples.

NTNFC Early Career Award: This project involves studying improvements to precision and detection limits for U isotopic measurements of particles. Results from that work will inform measurement protocols used in this proposed study.

Technology Readiness Level

Technology Readiness Level Table

Start TRL	End TRL	Component(s)	Notes
7	8	LA-MC-ICP-MS actinide particle analysis protocol development	LA-MC-ICP-MS method development required for this purpose but well-documented methodology available in literature. Validation against sample analyzed by technique of choice, LG-SIMS.
6	8	Pu particle analysis by LG-SIMS and LA-MC-ICP-MS	Both LG-SIMS and LA-MC-ICP-MS instruments are capable of this measurement. Development work to novel application of environmental safeguards swipes.
6	8	Mixed U/Pu particle analysis by LG-SIMS and LA-MC-ICP-MS	Both LG-SIMS and LA-MC-ICP-MS instruments are capable of this measurement. Development work to novel application of environmental safeguards swipes.

Joule Metric

It is anticipated that on the successful completion of this work the newly developed capability could be incorporated into our NWAL analyses.

Helium-3 Allocation

Helium-3 will not be required.

Funding by Task

Project Budget Table

Task	LAB1 Estimated FY19 Carryover Funds ($K)	LAB1 New Funding Requested ($K)	Total Funding Needed ($K)	Total New Funding Requested ($K)
1	$99	$555	$1,369 Carryover + new funding	$1,221 Just new
1	0	100	100	100
2	0	200	200	200
TOTAL	0	300	300	300

Anticipated Future Needs and Activities

The work to analyze the mixed U/Pu particles by LG-SIMS and LA-MC-ICP-MS will be started in FY19 but additional funds in FY20 will be required to complete the work. Only LANL will be involved.

Year	New Funding ($K)	Anticipated Future Tasks
FY20	300	Preparation of mixed U/Pu particle mounts and analysis by LG-SIMS and LA-MC-ICP-MS.
FY21		

Mortgage Table

Conferences and Workshops

None are anticipated.

Students and Postdocs

None are requested.

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

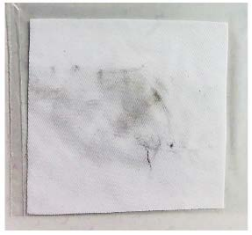
OFFICE OF NONPROLIFERATION AND ARMS CONTROL (NPAC)

INTERNATIONAL NUCLEAR SAFEGUARDS

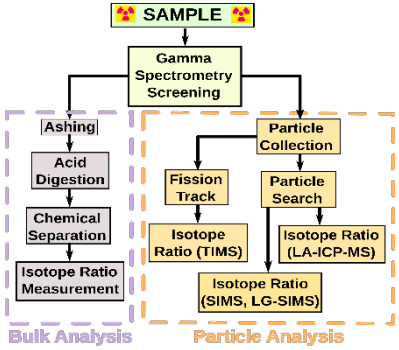
Plutonium particle analysis by LG-SIMS and LA-MC-ICP-MS for environmental safeguards

Your Project Tweet: Novel plutonium particle analysis techniques advance ability to verify treaty compliance

Background/State of the Art



- Environmental dust collected from nuclear facilities analyzed for treaty verification
- Currently analysis can be via bulk dissolution (U and Pu) or individual particles (only U) (see below).



Innovation

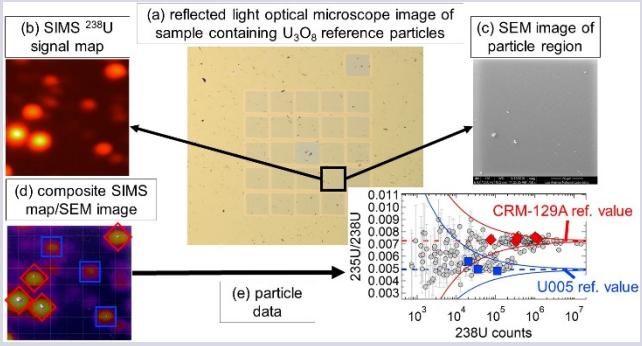
- Particle analysis is more powerful and can identify nuclear activities that are often undetectable if swipe is dissolved.
- Develop analysis protocols of **Pu** particles.
- Develop analysis protocols of mixed **U and Pu** particles.

R&R #: [Enter Review and Release No.]

Approach, Metrics and Outcomes

MAIN GOALS

- Improve actinide particle analysis protocols for LA-MC-ICP-MS in our NWAL laboratory
- Successful isotope analysis of Pu particles and U/Pu particles by LG-SIMS and LA-MC-ICP-MS. Produce similar results to our current U particle LG-SIMS capability (see below).



APPROACH

- Benchmark newly established LA-MC-ICP-MS actinide analysis protocols using particle samples already analyzed by LG-SIMS.
- Prepare and analyze Pu-only particle mounts by LG-SIMS and LA-MC-ICP-MS.
- Prepare and analyze mixed U/Pu particle mounts by LG-SIMS and LA-MC-ICP-MS.

ASSUMPTIONS, LIMITATIONS & CONSTRAINTS

- Attempts to measure mixed U/Pu particles will be based on successful measurements of Pu-bearing particles.

REVIEW & RELEASE NUMBER

Impact

- Plutonium isotopic analysis of particles in the presence of an environmental matrix.
- Implementation of LA-MC-ICP-MS in an NWAL laboratory.
- Addresses:
  - IAEA STR-385 T.2.R.6
  - SGAS-002
- **Start of FY TRL = 6**
- **End of FY TRL (Planned) = 8**

Goals/Action Plan

Current FY

- LG-SIMS operational for U particle analysis.
- LA-MC-ICP-MS requires actinide particle method development for U particle analysis

Future FY

- Prepare and analyze Pu and mixed U/Pu particle mounts by LG-SIMS and LA-MC-ICP-MS.

Team

LANL

Principal Investigator: Joanna Denton (jdenton@lanl.gov, 505-695-3705), Travis Tenner (tenner@lanl.gov, 505,664-0115)